# Theory and Modeling of Dielectric Materials

*Dielectric ceramics are widely used in applications such as semiconductor gate dielectrics, actuators, capacitors, and resonators or filters for microwave communications. For simple systems, first-principles (FP) methods allow direct calculations of low-temperature dielectric constants. For complex systems, and for rational new materials design, larger scale modeling is required. Multiscale effective Hamiltonian (EH) models derived from FP calculations retain high accuracy and allow phenomena caused by chemical ordering, defects, and changes in temperature to be explored. The EH provides a bridge from FP calculations (≤ 100 atoms) to the needed computations with hundreds of thousands of atoms. We are developing a methodology to enable automatic EH generation for real three-dimensional systems.*

**Eric Cockayne and Benjamin P. Burton**

Materials that are optimized for industrial applications are generally solid solutions in which the configuration of ions on mixed ion sites strongly affects the physical properties. To model these phenomena, detailed FP calculations are performed on a variety of perfectly ordered systems. For example, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is the main component of recently discovered materials with ultrahigh piezoelectric constants. PMN presents a singular challenge, because the details of Mg-Nb ordering are not fully known. To better understand PMN, we studied various PMN composition supercells with 15 to 30 atoms. A comparison of fully relaxed structures predicts a ground state ordering different from that previously assumed. The two lowest-energy structures found are most compatible with the "random site model" of PMN deduced from experiment. Calculated infrared spectra (directly related to the dielectric function) also show that the two lowest energy structures are most similar to experiment.

For the $(CaAl_{1/2}Nb_{1/2}O_3)_{1-x}$–$(CaTiO_3)_x$ (CAN-CT) system of microwave dielectric interest, a cluster expansion EH model for the low temperature dielectric constant was developed to calculate the dielectric constant for an arbitrary CAN-CT configuration as a function of x and Ti-Al-Nb ordering. Work is in progress to parameterize similar models for other solid solution systems.

Temperature dependent dielectric properties can be modeled with Monte Carlo and molecular dynamics simulations based on EHs. The EH for a heterovalent solid solution includes the random local electric fields generated by mixing differently charged ions in an alloy. We compiled a catalog of the possible local field directions in the nearest-neighbor approximation. By including local fields in an EH for $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), we can reproduce the experimental observation that the dielectric peak of PSN, as a function of temperature, is broadened when nanoscale ordered domains are present.

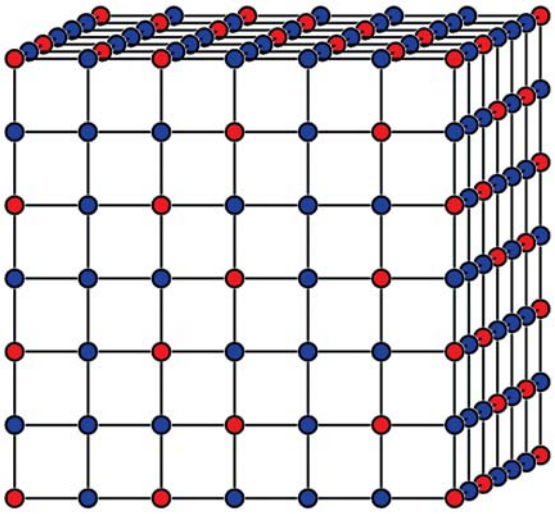

***Figure 1:*** *Predicted ground-state ordering of Mg (red) and Nb (blue) in $PbMg_{1/3}Nb_{2/3}O_3$.*

Defects also affect physical properties. We computed the dipole moment of a Pb-O divacancy in $PbTiO_3$ from FP. Its moment is 2.28 e times the distance between the original Pb and O sites. The large electric fields produced by such defects have been incorporated into our EH for PSN.

Effective Hamiltonians for dielectrics and ferroelectrics are based on an efficient "lattice Wannier function" (LWF) description of the lattice dynamics of these systems. We have found a principle for automatically generating LWF and have demonstrated that it works on one-dimensional model systems. The method works equally well for chemically ordered systems, disordered systems, and systems with defects. This is a highly promising step towards automatic generation of effective Hamiltonians for real three-dimensional systems, which will make these EH methods accessible to non-experts.

## Contributors and Collaborators

I. Levin, M. Lufaso, S. Tinte (Ceramics Division, NIST); P. Gehrig (NIST Center for Neutron Research, NIST); A. van de Walle (Northwestern U.); S.A. Prosandeev (Rostov State U.); U.V. Waghmare (JNCASR)